“Study of Structural and Dynamical Properties of Some Polymers and Biomolecules”

A pre-synopsis submitted to the

Swami Ramanand Teerth Marathwada University, Nanded

For the registration of

Doctor of Philosophy in Physics

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Study of Structural and Dynamical Properties of Some Polymers and Biomolecules

Introduction:

Polymers:

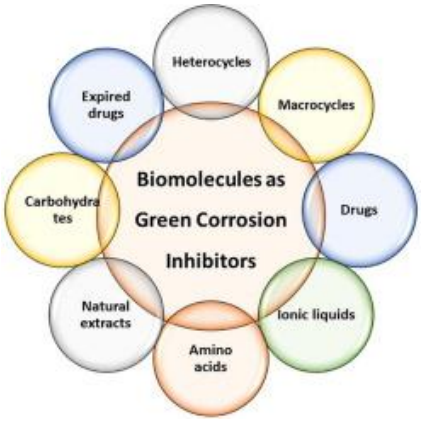
Polymers are materials made of long, repeating chains of molecules called as monomer. Monomer is the unit of polymer. The process of combination of unit molecule monomer to form larger molecule polymer is called as polymerization [1]. Number of monomer decides chain length of the polymer. Polymers have unique properties, depending on chain length, type of molecules being bonded and types of bonding etc. Properties of polymer can be determined mostly by using attractive forces present between polymer chains [2-4].Some polymers are soft and flexible while some are hard and tough. Polymers are of two types, natural polymer and artificial polymer composed of very large molecules, called macromolecules.

In the proposed study we are planning to study the interaction of polymers like poly ethylene glycol (PEG), poly propylene glycol (PPG), poly vinyl pyrollidone (PVP)…etc with different solvents at different frequencies using different spectroscopic techniques.

Biomolecules:

Biomolecules are the most essential organic molecules, which are involved in the maintenance and metabolic processes of living organisms. These organisms ranges from small molecules such as primary and secondary metabolities and harmones to large macromolecules like proteins, nucleic acid, carbohydrates,lipids etc.

Bio-molecules have broad range of application in various fields such as pharmaceuticals, physical chemistry, biology and industry.



Heterocyclic bioactive compounds:

Heterocyclic bioactive compounds are the compounds which constitutes the largest and most varied family of organic compounds. A heterocyclic compound has at least two different elements as a member of its ring. The most common hetero atoms found on a cyclic ring are oxygen, nitrogen and sulpher. Some Heterocyclic bioactive compounds behaves as a biomolecules as shown in above diagram.

Classification of Heterocyclic bioactive compounds:

Based on electronic arrangements we can classify Heterocyclic bioactive compounds into two types:

1. Aliphatic heterocyclic bioactive compounds
2. Aromatic heterocyclic bioactive compounds

Aliphatic Heterocyclic bioactive compounds are those cyclic heterocycles that do not contain any double bond. Example of aliphatic heterocyclic bioactive compounds are Aziridine, Ethylene Oxide, thirane, Oxetane, pyrrolidone, piperidine, etc.

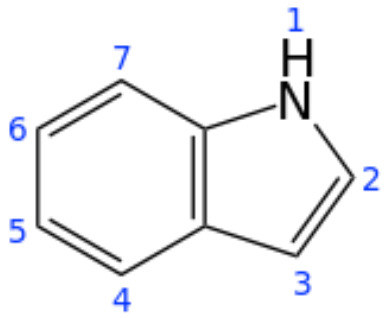
Aromatic heterocyclic biomolecules, as the name suggests, are cyclic aromatic compounds. Aromatic heterocyclic bioactive compounds are analogous to benzene. Examples Furan, Pyrrole, thiophene, indole, Benzofuran, Carbazole, Quinoline, Oxazole, Pyrazole, Pyridazine, Pyrimidine etc.

Based on the structure, we can classify heterocyclic bioactive compounds into five types, i.e. three-membered, four-membered, five-membered, six-membered and condensed or fused heterocyclic biomolecules.

In present work we are studying some derivatives of six- membered heterocyclic biomolecules. These heterocyclic bioactive compounds are derived from benzene by replacing one of the carbon with a hetero atom having a lone pair of electrons.

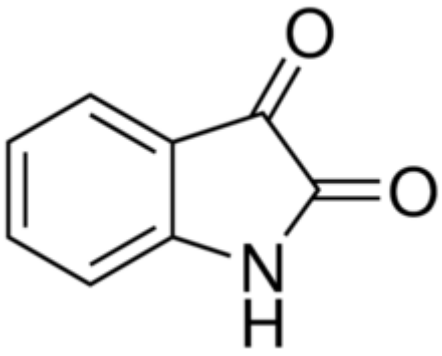
In present work we are studying three types of heterocyclic bioactive compounds shown below.

1. Indole.



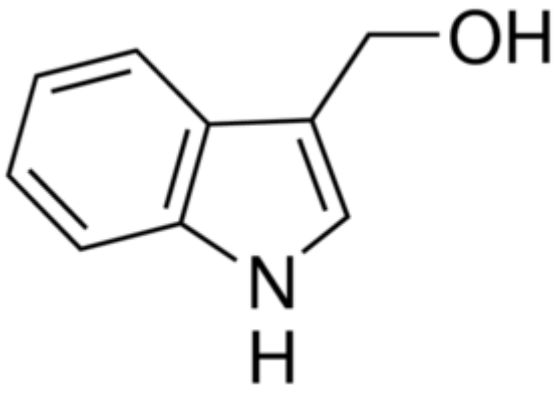
Indole (C_8H_7N) is an aromatic heterocyclic bioactive compound having molecular formula C_8H_7N. It has a bicyclic structure, consisting of a six-membered benzene ring fused to a five-membered pyrrole ring. Spectroscopic studies of indole are of interest when investigating the nature of the environment of tryptophan residues in model polypeptides and proteins.

2. Isatin



Isatin (1H-indole-2, 3-Dione) ($C_8H_5NO_2$), also known as indenedione and indole quinone. It has one nitrogen atom and two carbonyl groups. It is made up of two cyclic rings, one with six members and the other with five, both of which are planar. Aromatic character is found in the six-membered ring, while anti-aromatic character is found in the five-membered ring.

3. Indole 3- carbinol



Indole-3-carbinol (C_9H_9NO) is produces by the breakdown of the glucosinolate glucobrassicin, ehich can be found at relatively high level in cruciferous vegetables such as brocalli,cabbage,cauliflower and kale. Indole-3-carbinol is the subject of on-going biomedical research into its possible anticarcinogenic, antioxidant and anti atherrogenic effects.

Applications of heterocyclic bioactive compounds:

1. Heterocyclic bioactive compounds are used in agrochemicals and pharmaceuticals industries.

2. Heterocyclic bioactive compounds are used as starting material in the synthesis of organic compounds.

3. Heterocyclic bioactive compounds are used in corrosion inhibitors, sanitisers, anti-ordinates and developers.

4. Heterocyclic bioactive compounds are used in pesticides, dyes and plastics.

Various techniques are available in order to investigate structural properties of biomolecules that can find appropriate use in diverse field. Electromagnetic frequencies in the GHz range are increasingly applied in biotechnology and medicine. In order to fully exploit both their potentials and risks detailed information about the dielectric properties of biological material is needed. Attempts have been taken previously by many researchers in order to study chemical, physical, and biological properties of Heterocyclic bioactive compounds.

Abstract of proposed work plan/ problem

In the proposed research work we are planning to perform temperature and concentration dependent dielectric properties of different Heterocyclic bioactive compounds such as indole, isatin, indole 3- carbinol with DMSO at frequency in the range of 10MHz-50GHz at different concentration using Time Domain Reflectometry technique (TDR). The dielectric parameters like static Dielectric constant, Relaxation time, Effective Dipole moment,, hydration number, Kirkwood factor (g) and effective volume Veff and thermodynamic parameters such as Enthalpy, Entropy and Free energy will be calculated and expressed in terms of molecular interaction..

Review of Literature and Development in the subject (Previous work done in the relevant area):

Dielectric relaxation study of heterocyclic bioactive compounds such as pyrrolidone, piperidine and 2- acetylpyridine in highly viscous media i.e. paraffin oil and paraffin oil+ cyclohexane mixtures at 294 K-318 K have been carried out by Rajni et al and concluded that, the dielectric relaxation of polar solute occurs from the rotational diffusion which require a co-oprative motion of the solvent molecule forming the cage around the solute molecule. [5] J crosseley and s. walker studied molecular relaxation of some heterocyclic amines in dilute solution to calculate relaxation time and dipole moments for pathalazine, quinoline and isoquinoline in cyclohexane at 50^0 C concluded that, when the molecular interaction is minimized, indicates there is hardly any variation of relaxation time by varying the direction of the molecular dipole in these three molecules of almost identical size and shape. [6]

According to the data compiled by N. K. Mehrotra, dielectric relaxation mechanism in five Heterocyclic bioactive compounds in dilute solutions using microwave technique was reported. Measurements have been made at different temperatures to calculate dipole moments and free energies of activation for the process of dipole orientation and viscous flow. It has been observed that the relaxation time is very closely related with the molecular parameters, such as size, shape and nature of the solute molecule. [7]

Though many attempts has been made to investigate large numbers of heterocyclic bioactive compounds but no study has found to glance through the structural behaviour of Indole, Isatin and indole 3- carbinol molecules in different solvents. As mentioned DMSO is an excellent solvent and is having a range of pharmacological activity and ability to penetrate biological membranes. Therefore, In the proposed study dielectric and thermo dynamical properties of Indole, Isatin and indole 3- carbinol in different solvents will be investigated using Time domain reflectometry technique in the frequency region of 10 MHz-50 GHz at different temperatures ranging from 298.15 K- 273.15 K which is still the subject of interest.

Objectives of Research/ Proposed Hypothesis:

In the proposed work, we focus on the concentration and temperature dependence of structural and dynamical properties of Heterocyclic bioactive compoundssuch as indole, Isatin and indole 3 carbinol in the solution state with different solvents.

Experimental setup

Time Domain Reflectometry (TDR) is used to describe a technique of observing time dependence reflection response of sample under study. H Fellner-Feldegg [8] first

developed it for measurement of loss and permittivity at very high frequency range. Time domain reflectometry is prepared to suitable fast rising pulse is applied to a transmission line, usually a co-axial line with 50Ω impedance. A co-axial line is connected to sampling device (sample holder). The schematic block diagram of the experimental setup for TDR [9-11] is shown in Figure 1.

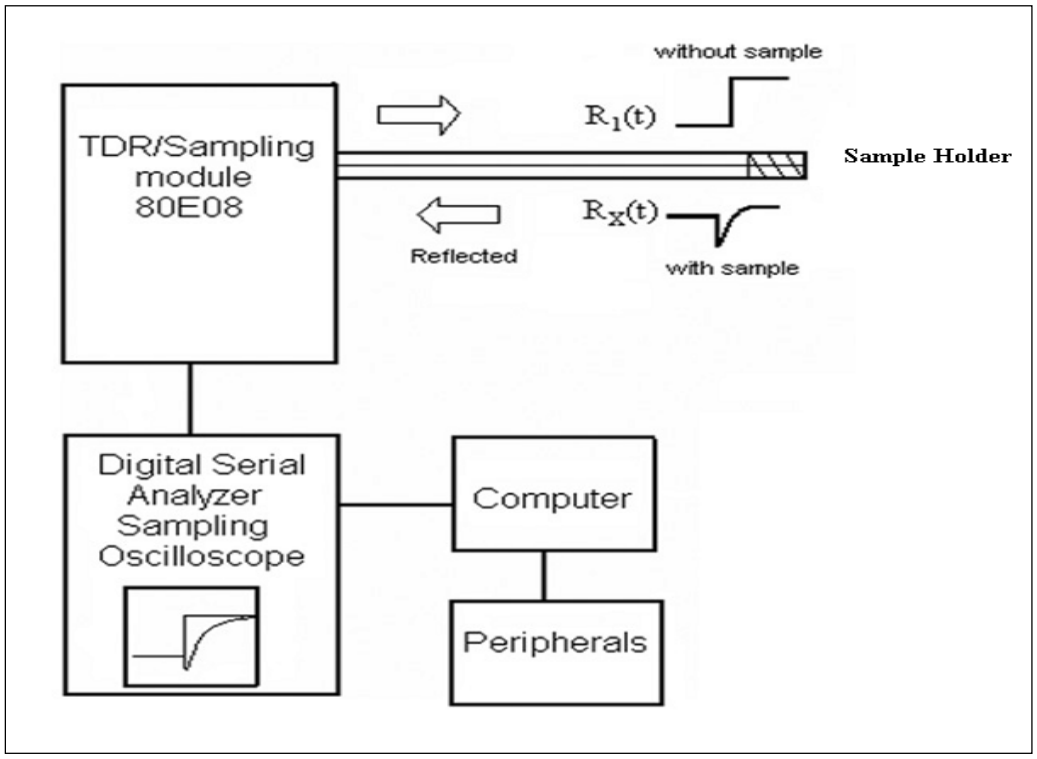


Fig.1: Schematic diagram of TDR.

In the basic TDR system a fast rising step voltage is propagated in an ideal coaxial line. The shape of step voltage remains unchanged as long as the propagation properties of the coaxial line remain the same. The complex permittivity of sample liquid is determined through Fourier transforming of the measured step pulses in the frequency range 10 MHz to 50 GHz.

The frequency dependence of the dielectric complex permittivity data obtained will be fited in to Havriliak-Negami [12] equation using non-linear least squares fit method.

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{[1+(j\omega\tau)^{1-\alpha}]^\beta} \qquad (1)$$

where ε_0 is the static dielectric constant, ε_∞ is the dielectric constant at high frequency, τ is relaxation time in ps., α and β are the distribution parameters. The Havriliak-Negami equation includes three relaxation models. The Debye model (α=0 and β=1) suggest a single relaxation time while the Cole-Cole ($0 \leq \alpha \leq 1$ and β=1) and Cole-Davidson (α=0 and $0 \leq \beta \leq 1$) models both suggest a distribution of relaxation times.

The complex dielectric spectra of bio-molecules are typical example, major result of the fitting procedure was that for all the investigated solutions a superposition of two Debye relaxation process

$$\varepsilon^*(\nu) = \frac{\Delta\varepsilon_1}{1+i2\pi\nu\tau_1} + \frac{\Delta\varepsilon_2}{1+i2\pi\nu\tau_2} \qquad (2)$$

For the study of multistep relaxation of molecular level mixture the generalized Cavell equation[13] relates the the observed relaxation streangth $\Delta\varepsilon_j$ of the j- relaxation process with both the molar concentration of the species (c_j)and its effective dipole moment μ_{eff} j through

$$\Delta\varepsilon_j = \frac{\varepsilon_s}{3(\varepsilon_s + (1-\varepsilon_s)A_j} \frac{N_A}{k_B T\varepsilon_0} \frac{\mu^2{}_{effj}}{(1-\alpha_j f_j)^2} c_j \qquad (3)$$

Where $\boldsymbol{\varepsilon}_s$ is the static permittivity, NA is Avogadro's number, kB the Boltzmann constant and T the temperature. Aj is the shape parameter of the reaction field and accounts for the shape of the relaxing particle [14,15] Concerning the reason of the changes in correlation between dipoles it has been proposed that they are due to a weakening of the solvent shielded layer among the heterocyclic molecules via growth of solute induced interaction

at higher concentration and we can obtain effective hydration number Z_{ib}. Z_{ib} is a dynamical hydration number which reflects the number of solvent molecules effectively locked by the solute.

$$Z_{ib} = \frac{c_W(c) - c_W{}^{app}(c)}{c} \qquad (4)$$

From the measured relaxation time τ_1 it is possible to calculate the effective volume of rotation and the viscosity η for the studied system using Stockes-Einstein-Debye equation [14],

$$V_{eff}\,\eta = [\tfrac{2\varepsilon_1+\varepsilon_{\infty},1}{3\varepsilon_1}]\tfrac{K_BT}{3}\,\tau_1 \qquad (5)$$

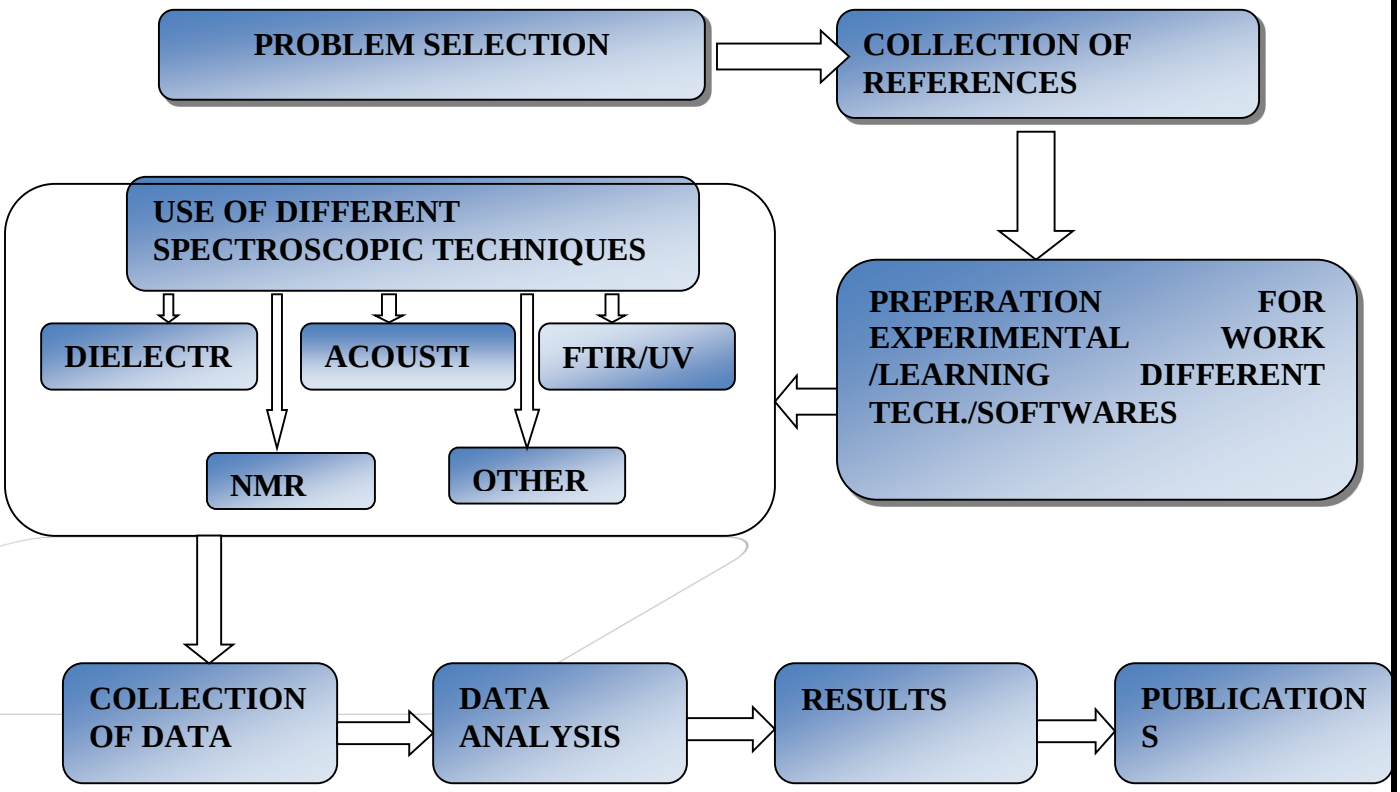
Where, ε_1 is dielectric constant for low frequency process, ε_{∞}, 1 is the high frequency limit of low frequency process which is associated to solute which can be calculated as, ε_{∞}, 1= $\Delta\varepsilon_2+\varepsilon_{\infty}$, K_B is Boltzmann's constant, T is temperature and τ_1 is relaxation time for low frequency process.

The thermodynamic parameters enthalpy (ΔH) and entropy (ΔS) will also be calculated using Eyring equation [16]

$$\tau = \frac{h}{k_BT}\exp\left(\frac{\Delta G}{RT}\right) \qquad (6)$$

Where, τ is the relaxation time in ps and T is the temperature in K and h is the Planck's constant. The enthalpy of activation gives information to the molecular energy involved in the relaxation process. The magnitude of ΔH indicates the overcome of a barrier equivalent in energy for the breakage of hydrogen bond in a liquid.

Proposed work Plan/ Formulation and Structure of Study:



Year-wise plan of work and targets to be achieved

Year/months	Target to be achieved
1-2 months	Collection of References and literature in continuation of my work
3-5 months	Experimental work
6-12 months	Analysis
13-18 months	Project completion Report, Publication, Communication etc.

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Signature of the student **Signature of the Guide**

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